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FIFTH QUARTERLY PROGRESS REPORT

HIGH TEMPERATURE THERMOELECTRIC RESEARCH

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FOREWORD

This report describes work performed under Contract AF 33(657)-7387, Project No. 8173, Task No. 817302-9 during the period 1 January 1963 - 29 March 1963. The contract concerns development of a high temperature thermoelectric generator, and is under sponsorship of the Flight Accessories Laboratory, Directorate of Aeromechanics, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio. For the Air Force, Mr. Charles Glassburn is project engineer.

The contract is being performed by Monsanto Research Corporation at its Dayton Laboratory with C. M. Henderson as project leader. Working with him are R. G. Ault, Emil Beaver, H. Jankowsky, R. Janowiecki, L. Reitsma, and G. H. Ringrose. Technical assistance was provided by R. R. Hawley, C. D. Reinhardt, D. Sevy and D. Swihart.

ABSTRACT

An experimental model 5-watt (nominal) generator completed 2556 hrs of a sustained performance test at a hot-end temperature of 1200 °C (+25 °C-4 °C), cold end at 714 °C (+12 °C-0 °C), in a vacuum of 10^{-5} - 10^{-6} mm Hg without degradation in power producing characteristics. The power/weight ratio of this generator, exclusive of heat source, ranged from 2.70 to 2.86 watt/lb. Tests at 1300 °C and higher temperatures will be attempted with this generator.

Graphite-ended segmented modules of n- and p-type thermoelectric materials to supplement p-type MCC 50, the thermoelectric material used in the 5-watt generator, were fabricated and partially evaluated. The first such p-n couple produced 250% more power than the p-type MCC-molybdenum couple used in the 5-watt generator. Improved emissive coatings and lightweight junctions between modules were produced. These developments suggest that an advanced experimental 50-watt generator having a power/weight ratio of 10-20 watt/lb is feasible.

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I. INTRODUCTION AND SUMMARY

A. BACKGROUND

The over-all program objective is to conduct applied research to establish the technical feasibility of utilizing a high temperature thermoelectric generator with a nuclear reactor heat source to produce a long-lived power supply for aerospace vehicles. This effort, the second phase of a program initiated 1 October 1961, is directed toward improving and further defining high-temperature thermoelectric generator components. The results are to be used to design and fabricate an advanced experimental model of a nominal 50 watts output suitable for evaluation by means of electrical heaters or a simulated loop of a liquid-metal-cooled nuclear reactor.

Research on several phases is proceeding simultaneously. These are:

Phase I - Experimental Model Evaluation The nominal 5-watt experimental generator, fabricated and preliminarily tested under the first year's effort, is being subjected to a sustained performance evaluation of 2500 hr with a hot junction temperature (T_h) of 1200 °C in a vacuum of 10^{-5} - 10^{-6} mm Hg. The cold junction temperature is about 700 °C, dependent upon the cooling available from radiation to ambient room temperatures. The generator is to produce power for an approximately matched electrical resistance load during this performance test.

Phase II - Component Improvement and Evaluation MCC 50, used in fabrication of the 5-watt generator, is available only as a p-type thermoelectric material. An n-type material, to supplement p-type MCC 50 in the temperature range of 700 °C - 1200 °C, plus other supplementary n- and p-type materials are necessary if substantial improvements in thermal efficiency and other characteristics are to be attained for the 50-watt generator. The new materials are to be developed by extending information resulting from the first year's efforts, and also by use of new proprietary thermoelectric materials. The latter are to be further developed on this project.

Effort will also be directed toward developing techniques for producing thermoelectric modules by new junction or end-forming methods. Plasma-arc spray coating the thermoelectric materials, as well as the electrical and thermal contacts, will be investigated. In addition, improved formulations will be screened, with the best formulations to receive a sustained evaluation.

Phase III - Advanced Experimental Model The design of this generator will be based on results of the first two phases of this project. A 50-watt advanced experimental model is to be fabricated after approval of the design by ASD.

B. SUMMARY

The experimental model 5-watt (nominal) generator completed 2556 hrs operation at a T_h of 1200 °C (+25 °C-4 °C) in a vacuum of 10^{-5} - 10^{-6} mm Hg without degradation of power producing characteristics. Power/weight ratios of 2.7 to 2,86 watts/lb, exclusive of heater and external circuitry, were obtained. Further tests at 1300 °C and higher temperatures are planned. The generator is based on MCC 50, a p-type thermoelectric material, coupled with molybdenum.

Improvement of proprietary n- and p-type thermoelectric materials (complementary to p-type MCC 50) and methods for joining them progressed to the point where segmented n- and p-type modules were fabricated and partially evaluated. An initial p-n couple, consisting of a graphite-ended segmented module of p-type MCC 50 joined with p-type MCC 40 coupled with a graphite-ended segmented module of n-type MCC 60 with n-type MCC 40, produced 250% more power at 1200 °C (T_h) than the MCC 50-molybdenum couples used in the experimental 5-watt generator when operated at the same approximate T_h and temperature differential (ΔT). In addition, an improved emissive radiator coating was developed which produced an increase of 40 °C in the ΔT in the modules of the experimental model generator operated at 1200 °C T_h. Progress was also made in the development of plasma-arc techniques for fabricating lightweight junctions for use between p- and n-type modules. These developments indicate that power/weight ratios in the range of 10-20 watts/lb will be possible for the advanced experimental model generator.

II. RESEARCH AND DEVELOPMENT RESULTS

A. PHASE I EXPERIMENTAL MODEL EVALUATION

This phase concerns the reliability and durability of the experimental model generator. The characteristics of the generator were to be evaluated by subjecting it to a sustained exposure for 2500 hrs at T_h of 1200 °C (+25 °C-4 °C) and a vacuum of 10^{-5} mm Hg. The generator completed 2556 hrs operation this quarter, meeting an important project requirement. During the sustained performance test the power output of the generator not only remained stable but actually increased somewhat ($\sim$8%) during the test period.

A cutaway assembly view, with partial cross sections, of the 5-watt generator as used for the sustained performance test is presented in Figure 1. All thermoelectric modules of the 3-module sections 1 through 9 around the central resistance heater unit and in the 3-module section on top of the generator consisted of 1/2" diameter by 1/2" long p-type MCC 50 elements capped with graphite hot and cold junctions. These modules were joined with molybdenum to form the basic p-n couple of the generator. Details of module and section construction are described in preceding quarterlies and the final report (ASD-TDR-62-896).

The hot junction temperature was controlled by feeding the output of the thermocouple located at the cold end of module B of the 3-module section 5 of Figure 1 to a power and temperature monitored control system shown in the circuit diagram of Figure 2. Thermocouples were located at three hot-end sites and five cold-end sites on five different 3-module sections, in order to obtain representative hot and cold temperatures of the generator under the test. The output of all temperature sensing thermocouples, generator current, and voltage outputs were continuously recorded. Throughout the test, the generator output, as indicated in Figure 2, was series-connected with a closely matched external resistive load "R" for maximum power output.

Prior to the 2500-hr test, the experimental model was subjected to more than 100 hrs of continuous operation and for 106 thermal cycles. These tests are described in the final report for the first year's work, ASD-TDR-62-896. After these tests and before initiating the sustained performance test, the experimental model was disassembled, inspected and reassembled. Close examination of each of the modules, prior to starting the sustained performance test, revealed no evidence of deterioration or physical damage (e.g., cracking) to the carbon-MCC 50-carbon modules. The molybdenum wire leads were also unaffected. The thermal insulation used to reduce the heat losses between the modules was discolored and somewhat embrittled, but seemingly functional. New insulation was used in the reassembly. It was noted that reinsertion of the molybdenum lead wires into the hot junction shoes of each three-

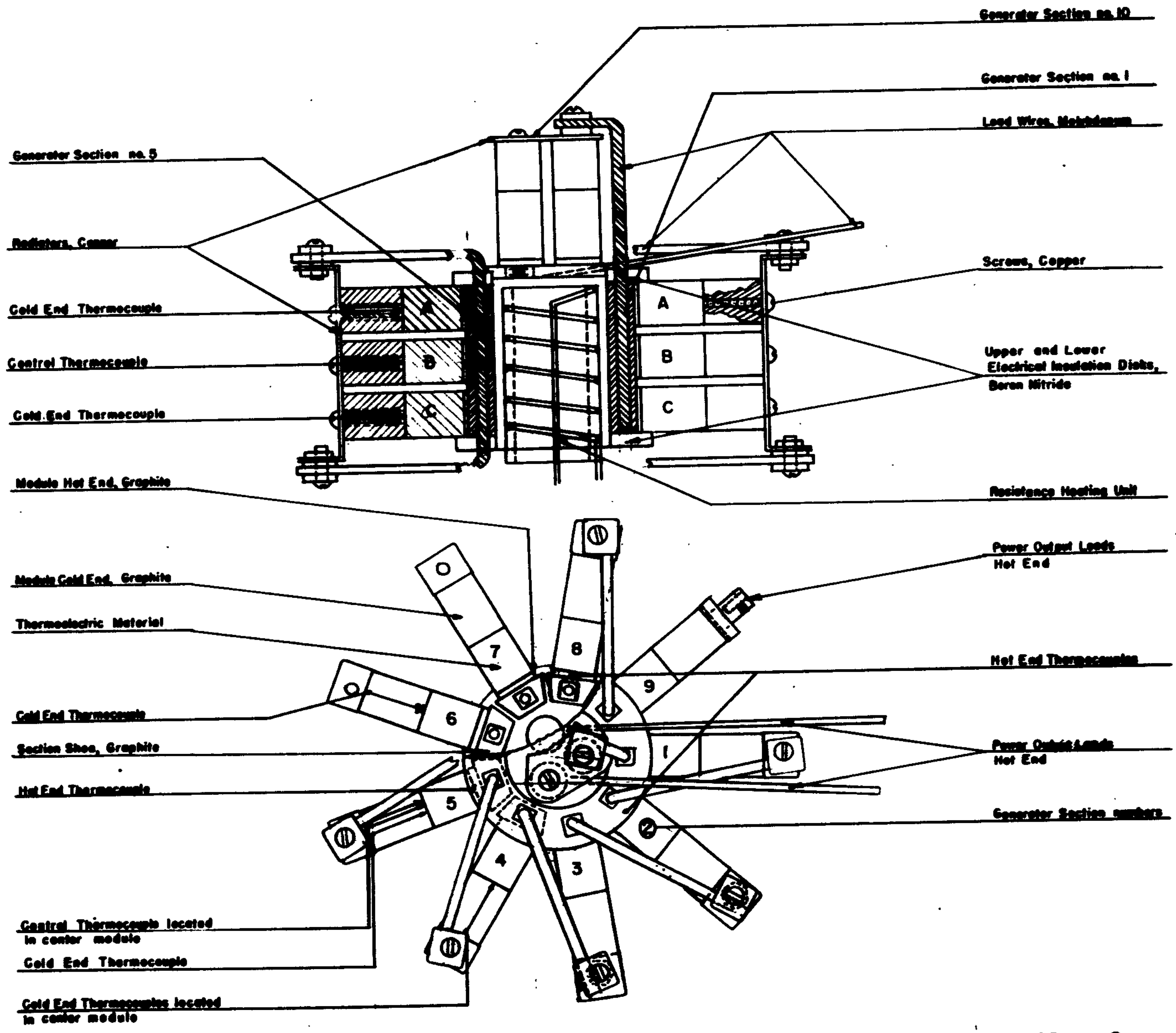


Figure 1. Arrangements of heater element, thermocouples and construction details of 5-watt experimental model generator for 2500-hr duration test. (Thermal insulation between modules not shown).

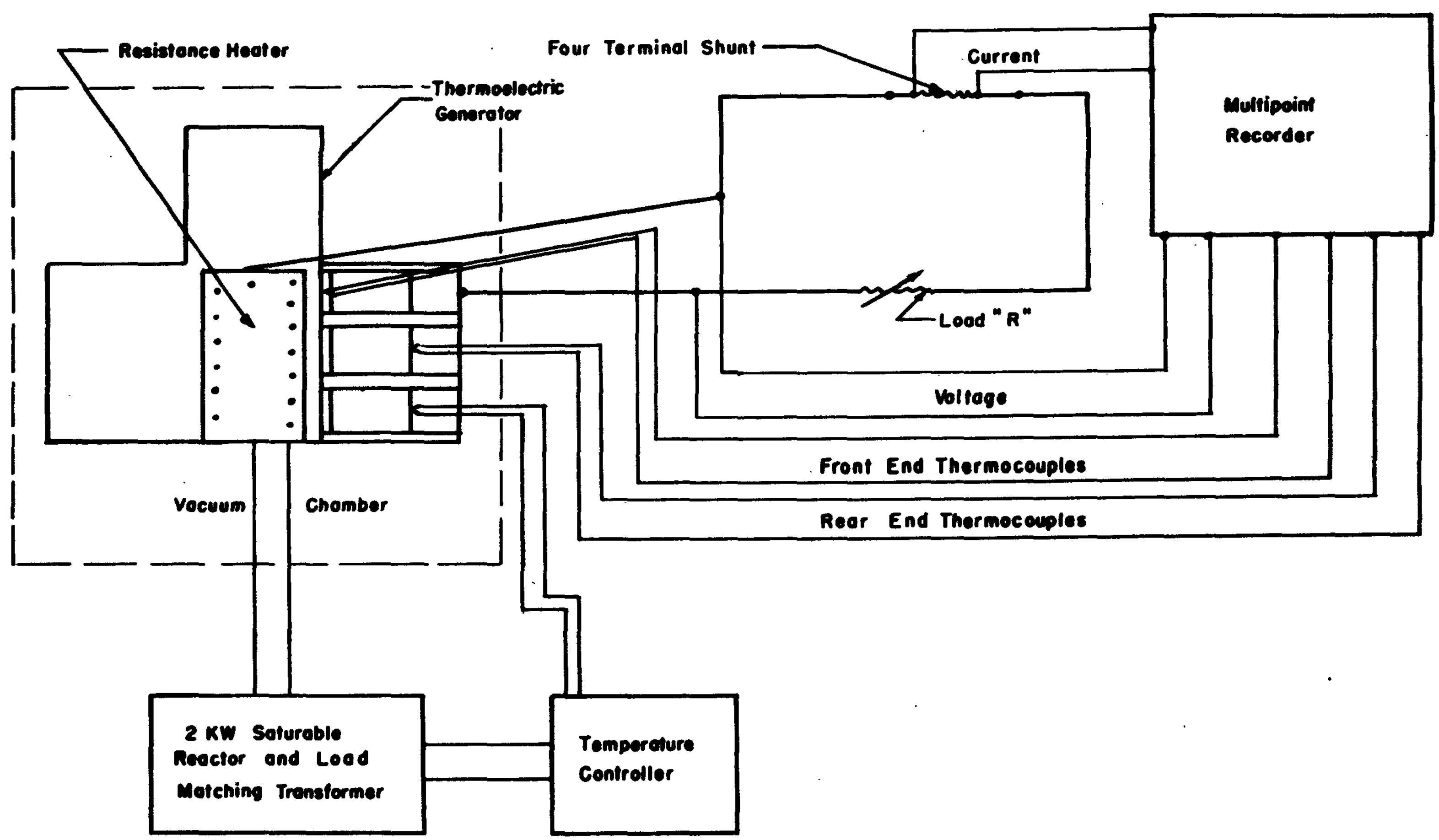


Figure 2. System for monitoring and controlling conditions of the model generator during the 2500-hr test.

module section caused a slight loosening of the fit between the wire and the hole in the graphite sections.

To offset an expected decrease in power output resulting from this somewhat loose fit between the molybdenum wire leads and the holes in the graphite section pieces, a tenth 3-module section was added in series with the nine 3-module sections used in the original generator. Thus assembled, and as shown in Figure 3, the experimental model generator weighed 1.6 lbs, exclusive of heat source and external lead wires.

The environmental vacuum chamber and auxiliary apparatus used to monitor generator performance during the 2500-hr test was described in the Fourth Quarterly Progress Report, pages 6-7.

Target conditions and data to be accumulated for the sustained performance test were as follows:

1. Hot-end temperature of about 1200°C.
2. Cold-end temperatures dependent upon radiation cooling.
3. Vacuum of 10^{-5} mm Hg.
4. Operation under approximately matched load conditions.
5. Environmental and operating conditions plus load voltage and current data to be recorded at least once each 24-hr period.

Data from the 2556 hrs test, during which at least two sets of data were collected for each 24-hr operating period, are presented in Table 1. Figure 4 is a plot of the data in Table 1. After some initial variations of power output, caused by small fluctuations of hot-end temperature, the power output of the generator slowly increased with time until at about 800 hrs it was 4.362 watts at a T_h of 1214°C and a ΔT of 487°C. This is approximately 8% more power than the 4.031 watts (2.5 watt/lb) the generator delivered at the start of the test and corresponds to a 2.7 watt/lb ratio of power output to generator weight. The generator output continued to increase slowly with time until at 1260 hrs operation the output was 4.588 watt at a T_h of 1220°C and a ΔT of 485°C, for a 2.86 watt/lb ratio and an approximate 14% improvement in generator output. Operation from 636 hrs to 2186 hrs was uninterrupted by heater trouble, the cause of six generator shutdowns during the first 636 hrs of the test.

A sudden drop in generator output voltage and power at the 2186th hour was traced to short circuiting of 2 or more of the 3-module sections by wires from the heater unit which apparently had vibrated loose from its moorings and leaned against the hot end of the generator. This trouble was cured by cooling the generator to room temperature and repositioning the heater. No further heater or generator trouble was encountered and the generator output remained relatively constant to the end of the test. After 2556 hrs operation the generator output had reached a plateau of 4.335 watts at 1212°C T_h and a ΔT of 462°C. It is believed that this improvement of 8%

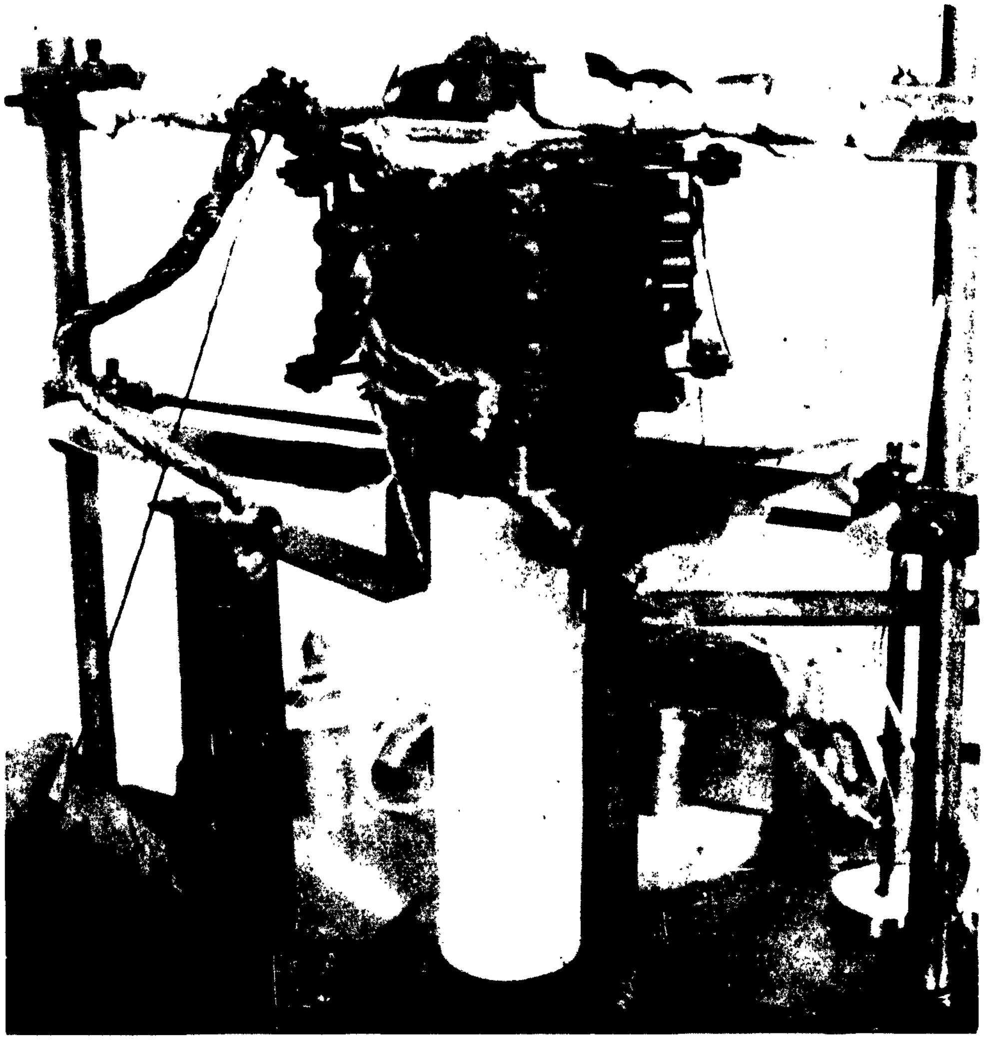


Figure 3. Experimental model generator mounted and ready for duration testing.

Table 1. DATA FROM 2500 HR HIGH TEMPERATURE TEST ON EXPERIMENTAL MODEL THERMOELECTRIC GENERATOR IN A VACUUM

Hours Operation	Average Hot End Temperature, °C	Average Cold End Temperature, °C	ΔT, °C	Generator Output Under Approximately Matched Load: Current, amp.	Potential, mv.	Power, watts	Internal Resistance, ohms	Open Circuit Potential mv.	Average Seebeck Coefficient, μv/°C	Vacuum, mm Hg x 10^{-5}
	1214	724	490	6.68	603	4.031	.0873	1187	242.0	2.0
	1208	719	489	6.57	597	3.920	.0896	1186	242.5	1.5
24	1219	722	497	6.91	600	4.150	.0862	1189	241.6	1.1
	1210	720	490	6.81	596	4.050	.0875	1186	242.0	.9
48	1221	727	494	6.87	602	4.140	.0860	1193	241.4	.85
	1215	724	491	6.95	588	4.000	.0863	1188	241.9	.95
72	1209	721	488	6.66	593	3.950	.0890	1186	243.0	.91
	1218	725	493	6.77	601	4.070	.0870	1190	241.3	.94
96	1213	722	491	6.91	587	4.050	.0869	1188	241.9	.87
	1219	726	493	6.88	604	4.160	.0860	1196	242.5	.85
120	1211	722	489	6.71	597	4.010	.0878	1187	242.7	.80
	Week end shutdown. Generator cooled to room temperature.									
	1214	727	487	6.75	599	4.040	.0873	1189	244.1	1.5
144	1217	726	491	6.81	601	4.090	.0870	1194	243.7	.88
	1222	727	495	6.89	605	4.170	.0859	1197	241.8	.90
168	1218	726	492	6.87	602	4.130	.0863	1195	242.8	.86
	1214	725	489	6.82	594	4.050	.0870	1188	242.9	.80
192	1209	721	488	6.70	590	3.950	.0891	1187	243.2	.91
	1220	726	494	6.87	604	4.150	.0861	1196	242.1	.94
216	1216	724	492	7.00	587	4.100	.0865	1193	242.4	.92
	1208	718	490	6.72	585	3.930	.0895	1187	242.2	.87
240	1213	722	491	6.88	587	4.040	.0874	1189	242.1	.83
	Week end shutdown. Generator cooled to room temperature.									
	1221	726	495	7.01	592	4.150	.0863	1197	241.8	1.3
264	1223	726	497	6.92	605	4.180	.0858	1199	241.2	.96
	1219	725	494	6.88	601	4.130	.0864	1196	242.1	.93
288	1212	723	489	6.86	593	4.060	.0870	1190	243.3	.91
312	1217	724	493	6.94	595	4.120	.0863	1194	242.1	
314	Resistance heater failed. Generator cooled to room temperature, heater unit replaced and generator brought back to temperature in 12 hour period.									
	1223	722	501	6.61	592	3.910	.0893	1182	237.0	2.4
324	1220	722	498	6.28	606	3.810	.0928	1189	237.0	1.05
	1214	723	491	6.68	603	4.028	.0873	1187	241.7	.98
348	1208	719	489	6.57	597	3.920	.0896	1186	242.0	.93
	Week end shutdown. Generator cooled to room temperature.									
	1196	714	482	6.27	596	3.730	.0928	1178	244.5	1.20
372	1214	721	493	6.57	605	3.970	.0925	1213	246.2	.98

Table 1., (Cont'd) **DATA FROM 2500 HR HIGH TEMPERATURE TEST ON EXPERIMENTAL MODEL THERMOELECTRIC GENERATOR IN A VACUUM**

Hours Operation	Average Hot End Temperature, °C	Average Cold End Temperature, °C	ΔT, °C	Generator Output Under Approximately Matched Load: Current, amp.	Potential, mv.	Power, watts	Internal Resistance, ohms	Open Circuit Potential mv.	Average Seebeck Coefficient, μv/°C	Vacuum, mm Hg x 10^{-5}
396	1209	721	488	6.63	604	4.010	.0903	1203	246.4	.96
	1209	722	487	6.60	604	3.990	.0908	1203	246.8	.97
420	1209	721	488	6.67	605	4.030	.0898	1204	246.9	.94
	1216	724	492	6.71	622	4.170	.0886	1216	247.0	.90
444	1215	725	490	6.62	605	4.010	.0921	1215	248.0	.88
	1212	724	488	6.67	622	4.150	.0885	1213	248.6	.86
468	1214	727	487	6.775	628	4.256	.0869	1218	249.9	.80
	1212	725	487	6.740	629	4.240	.0881	1223	251.0	.80
492	1208	724	484	6.73	618	4.160	.0892	1218	251.8	.80
	1210	726	484	6.765	622	4.210	.0882	1219	251.8	.80
516	1211	726	485	6.755	625	4.220	.0884	1223	251.8	.80
	1208	725	483	6.625	631	4.180	.0886	1218	252.5	.8
518	1202	724	478	6.79	610	4.140	.0885	1211	253.2	.7
	Resistance heater failed. Generator cooled to room temperature, heater unit replaced and generator brought back to temperature in 12 hour period.									
540	1208	720	480	6.75	612	4.130	.0930	1240	254.2	1.8
564	1208	720	488	6.752	615	4.150	.0928	1242	254.3	.98
	1205	719	486	6.71	615	4.130	.0939	1245	255.2	.95
588	1207	720	487	6.765	614	4.155	.0932	1245	255.4	.85
	1207	721	486	6.76	618	4.180	.0909	1233	253.8	.84
612	1207	721	486	6.67	626	4.170	.0921	1240	255.0	.6
	1203	717	486	6.77	618	4.180	.0917	1239	254.9	.7
636	1202	717	485	6.79	621	4.219	.0898	1231	253.6	.7
	1205	717	488	6.83	624	4.260	.0905	1242	254.4	.9
			Week end shutdown. Generator cooled to room temperature.							
660	1208	717	491	6.84	625	4.274	.0915	1251	254.6	.98
	1206	721	485	6.80	620	4.215	.0910	1239	255.0	.85
684	1216	725	491	6.90	629	4.340	.0902	1252	255.1	.8
	1199	719	480	6.73	617	4.150	.0910	1229	255.1	.5
708	1207	723	484	6.81	627	4.269	.0902	1241	256.3	.7
	1209	723	486	6.885	622	4.285	.0908	1247	256.6	.7
732	1211	723	488	6.870	629	4.324	.09023	1249	256.2	.8
	1207	723	484	6.83	628	4.288	.09003	1243	257.0	.6
756	1208	723	485	6.80	629	4.274	.0899	1240	256.0	.6
	1206	723	483	6.79	630	4.275	.0904	1243	257.3	.7
780	1211	726	485	6.86	633	4.340	.0887	1241	256.2	.7
	1209	724	485	6.79	634	4.302	.0896	1242	256.2	.7
804	1212	725	487	6.735	648	4.362	.0885	1244	255.6	.78

Table 1., (Cont'd) **DATA FROM 2500 HR HIGH TEMPERATURE TEST ON EXPERIMENTAL MODEL THERMOELECTRIC GENERATOR IN A VACUUM**

Hours Operation	Average Hot End Temperature, °C	Average Cold End Temperature, °C	ΔT, °C	Generator Output Under Approximately Matched Load: Current, amp.	Potential, mv.	Power, watts	Internal Resistance, ohms	Open Circuit Potential mv.	Average Seebeck Coefficient, $\mu v/°C$	Vacuum, mm Hg x 10^{-5}
828	1210	725	485	6.69	646	4.320	.0895	1245	256.7	.70
	1210	725	485	6.97	622	4.330	.0895	1245	256.7	.63
852	1206	722	484	7.01	614	4.298	.0898	1243	256.8	.83
	1218	729	489	7.08	626	4.430	.0886	1254	256.4	.90
876	1211	725	486	7.05	618	4.360	.0893	1248	256.7	.85
	1223	730	493	7.15	628	4.484	.0898	1270	257.5	.88
900	1216	727	489	7.05	624	4.402	.0900	1259	257.6	.74
	1211	727	484	6.90	631	4.352	.0905	1255	259.0	.66
924	1211	727	484	6.87	632	4.339	.0907	1255	259.2	.75
	1210	727	483	6.90	634	4.372	.0894	1251	259.0	.62
948	1209	726	483	6.86	629	4.318	.0906	1252	259.2	.58
	1209	726	483	6.90	629	4.340	.0904	1253	259.4	.62
972	1213	728	485	6.92	633	4.379	.0902	1257	259.1	.60
	1209	727	482	6.93	629	4.358	.0898	1251	259.5	.50
996	1209	726	483	6.90	630	4.341	.0903	1252	259.3	.54
	1211	728	483	7.03	626	4.396	.0894	1254	259.9	.59
1020	1207	729	481	6.95	622	4.322	.0902	1249	259.7	.52
	1207	731	481	6.96	627	4.364	.0902	1255	260.8	.53
1044	1214	279	485	6.98	635	4.432	.0904	1266	261.0	.50
	1215	731	484	7.03	632	4.446	.0899	1264	261.2	.56
1068	1210	730	480	6.97	631	4.395	.0899	1257	262.8	.43
	1208	730	478	6.90	633	4.368	.0907	1259	263.3	.46
1092	1217	733	484	7.02	640	4.491	.0897	1270	262.5	.60
	1216	733	483	7.02	639	4.482	.0895	1267	262.3	.60
1116	1217	733	484	7.01	640	4.489	.0893	1266	261.6	.60
	1219	734	485	7.04	642	4.517	.0894	1271	262.0	.60
1140	1218	734	484	7.03	641	4.506	.0892	1269	262.2	.60
	1220	734	486	7.09	644	4.569	.0886	1273	262.0	.60
1164	1219	735	484	7.06	641	4.525	.0892	1270	262.5	.60
	1216	734	482	6.99	638	4.460	.0896	1264	262.3	.56
1188	1216	734	482	7.00	638	4.469	.0896	1265	262.6	.55
	1216	734	482	7.03	642	4.507	.0887	1265	262.5	.56
1212	1217	734	483	7.03	641	4.505	.0891	1268	262.5	.56
	1210	730	480	6.96	638	4.443	.0891	1259	262.3	.50
1236	1211	731	480	6.97	639	4.449	.0894	1261	262.7	.51
	1210	731	479	6.93	639	4.424	.0890	1255	262.0	.53

Table 1., (Cont'd) DATA FROM 2500 HR HIGH TEMPERATURE TEST ON EXPERIMENTAL MODEL THERMOELECTRIC GENERATOR IN A VACUUM

Hours Operation	Average Hot End Temperature, °C	Average Cold End Temperature, °C	ΔT, °C	Generator Output Under Approximately Matched Load: Current, amp.	Potential, mv.	Power, watts	Internal Resistance, ohms	Open Circuit Potential mv.	Average Seebeck Coefficient, μv/°C	Vacuum, mm Hg x 10^{-5}
	1211	731	480	6.94	640	4.442	.0891	1258	262.1	.54
1260	1220	735	485	7.10	646	4.588	.0880	1271	262.0	.68
	1221	736	485	7.11	643	4.573	.0887	1274	262.6	.68
1284	1213	734	479	7.02	639	4.486	.0894	1267	264.5	.64
	1211	734	477	6.98	637	4.448	.0892	1260	264.1	.63
1308	1208	733	475	6.93	633	4.385	.0899	1256	264.2	.49
	1207	732	475	6.92	633	4.378	.0896	1253	264.1	.49
1332	1207	733	474	6.90	634	4.377	.0900	1255	264.6	.53
	1209	732	477	6.92	635	4.397	.0898	1257	264.2	.53
1356	1218	736	482	7.04	642	4.517	.0891	1269	263.5	.57
	1215	736	479	7.02	640	4.493	.0888	1264	263.4	.57
1380	1206	732	474	6.85	640	4.381	.0894	1252	263.9	.48
	1207	732	475	6.86	640	4.393	.0896	1255	264.0	.41
1404	1201	730	471	6.82	632	4.310	.0899	1245	264.6	.38
	1200	730	470	6.82	632	4.307	.0896	1243	264.3	.38
1428	1212	735	477	7.09	630	4.464	.0890	1261	264.1	.54
	1211	735	476	7.10	631	4.478	.0886	1260	264.3	.54
1452	1208	733	475	7.02	630	4.420	.0889	1254	264.1	.48
	1208	733	475	7.02	630	4.424	.0887	1253	263.9	.48
1476	1207	731	476	6.99	631	4.410	.0897	1258	264.2	.46
	1207	732	475	6.94	625	4.337	.0908	1255	264.1	.46
1500	1211	735	476	7.04	634	4.463	.0883	1255	263.6	.54
	1210	735	475	7.03	634	4.456	.0882	1254	264.0	.54
1524	1209	733	476	7.00	635	4.445	.0887	1256	263.9	.48
	1209	733	476	6.99	634	4.431	.0886	1254	263.4	.62
1548	1209	730	479	7.10	633	4.494	.0891	1266	264.3	.52
	1208	733	475	7.04	629	4.428	.0899	1262	265.6	.60
1572	1208	733	475	7.04	629	4.428	.0897	1261	265.4	.60
	1210	735	475	7.05	630	4.441	.0879	1250	263.1	.69
1596	1209	734	474	7.04	629	4.428	.0882	1250	263.7	.65
	1214	736	478	7.08	630	4.460	.0896	1265	264.6	.58
1620	1215	736	479	7.09	630	4.466	.0898	1267	264.5	.68
	1208	738	470	6.96	620	4.315	.0890	1240	263.8	.43
1644	1212	735	477	7.12	635	4.521	.0883	1264	264.9	.43

Table 1., (Cont'd) **DATA FROM 2500 HR HIGH TEMPERATURE TEST ON EXPERIMENTAL MODEL THERMOELECTRIC GENERATOR IN A VACUUM**

				Generator Output Under Approximately Matched Load						
Hours Operation	Average Hot End Temperature, °C	Average Cold End Temperature, °C	ΔT, °C	Current, amp.	Potential, mv.	Power, watts	Internal Resistance, ohms	Open Circuit Potential mv.	Average Seebeck Coefficient, μv/°C	Vacuum, mm Hg x 10^{-5}
	1207	735	472	7.10	621	4.409	.0882	1247	264.1	.46
1668	1210	736	474	7.08	625	4.425	.0888	1254	264.5	.50
	1205	734	471	7.08	620	4.389	.0878	1242	263.6	.46
1692	1205	734	471	7.04	620	4.364	.0882	1241	263.4	.45
	1204	734	470	7.04	621	4.372	.0882	1242	264.2	.40
1716	1198	731	467	6.89	622	4.285	.0896	1240	265.5	.45
	1200	732	468	6.90	623	4.300	.0897	1242	265.3	.41
1740	1206	735	471	6.96	628	4.370	.0890	1248	264.9	.46
	1205	735	470	6.95	628	4.364	.0889	1246	265.1	.41
1764	1206	735	471	7.06	623	4.398	.0879	1244	264.1	.48
	1204	735	469	7.04	621	4.372	.0876	1238	263.9	.45
1788	1209	736	473	7.07	630	4.454	.0876	1250	264.2	.50
	1209	736	473	7.06	628	4.434	.0879	1249	264.0	.52
1812	1213	738	475	7.11	632	4.493	.0877	1256	264.2	.54
	1213	738	475	7.10	631	4.480	.0878	1255	264.1	.50
1836	1202	734	468	7.03	620	4.358	.0884	1242	265.3	.44
	1204	734	470	7.05	621	4.378	.0883	1244	264.6	.40
1860	1203	734	469	6.97	624	4.349	.0886	1242	264.8	.42
	1204	734	470	7.00	627	4.389	.0881	1244	264.6	.41
1884	1207	736	471	7.01	627	4.395	.0884	1247	264.7	.49
	1208	736	472	7.02	629	4.415	.0883	1249	264.6	.45
1908	1202	735	467	6.89	626	4.313	.0888	1238	265.0	.38
	1200	734	466	6.90	627	4.326	.0882	1236	265.2	.35
1932	1206	736	470	6.92	637	4.408	.0895	1245	264.8	.41
	1206	736	470	6.91	634	4.381	.0882	1244	264.6	.45
	1210	736	474	7.06	624	4.405	.0887	1250	263.7	.56
1956	1209	736	473	7.02	628	4.408	.0889	1252	264.6	.50
	1207	735	472	7.00	629	4.403	.0885	1248	264.4	.43
1980	1208	736	472	7.04	626	4.407	.0882	1247	264.1	.44
	1200	733	467	6.94	621	4.309	.0897	1243	266.1	.36
2004	1202	734	468	7.03	618	4.344	.0892	1245	266.0	.38

Table 1., (Cont'd) DATA FROM 2500 HR HIGH TEMPERATURE TEST ON EXPERIMENTAL MODEL THERMOELECTRIC GENERATOR IN A VACUUM

Hours Operation	Average Hot End Temperature, °C	Average Cold End Temperature, °C	ΔT, °C	Generator Output Under Approximately Matched Load: Current, amp.	Potential, mv.	Power, watts	Internal Resistance, ohms	Open Circuit Potential mv.	Average Seebeck Coefficient, μv/°C	Vacuum, mm Hg x 10^{-5}
	1208	736	472	7.07	624	4.411	.0879	1245	263.7	.42
2028	1206	735	471	7.08	622	4.404	.0880	1245	264.3	.40
	1207	736	471	7.09	620	4.396	.0881	1245	264.3	.42
2052	1205	734	469	7.06	617	4.356	.0883	1240	264.3	.41
	1210	737	473	7.07	627	4.433	.0876	1246	263.4	.51
2076	1211	737	474	7.03	628	4.414	.0875	1243	262.2	.53
	1205	734	471	6.99	622	4.347	.0880	1237	262.6	.39
2100	1207	736	471	7.06	624	4.405	.0879	1244	264.1	.42
	1209	736	473	7.02	628	4.408	.0878	1244	263.0	.38
2124	1206	735	471	7.10	619	4.395	.0881	1244	264.1	.37
	1204	734	470	7.07	618	4.369	.0880	1240	263.8	.35
2148	1206	736	470	7.07	621	4.390	.0878	1242	264.2	.36
	1203	734	469	7.04	617	4.343	.0883	1239	264.1	.32
2172	1203	736	467	6.81	629	4.283	.0850	1208	258.6	.40
2186	1214	741	473	6.76	615	4.157	.0745	1119	236.5	.58
Generator shut down to investigate cause of sudden drop in circuit voltage and power. Trouble traced to the resistance heater which vibrated out of position, electrically shorting two 3-module sections. Tests were resumed in 24 hours, using same resistance heater, after it had been repositioned.										
2196	1201	743	458	6.59	635	4.185	.0963	1270	277.2	.67
	1200	744	456	6.55	638	4.180	.0944	1257	275.6	.66
2220	1200	743	457	6.55	641	4.198	.0944	1259	275.4	.68
	1210	748	462	6.68	649	4.332	.0927	1268	274.4	.70
2244	1209	748	461	6.67	648	4.320	.0929	1267	274.8	.69
	1207	747	460	6.63	645	4.279	.0924	1258	273.4	.68
2268	1205	747	458	6.60	642	4.241	.0926	1254	273.7	.68
	1204	748	456	6.81	623	4.241	.0904	1239	271.7	.63
2292	1203	747	456	6.81	623	4.241	.0902	1237	271.2	.62
	1208	749	459	6.80	632	4.290	.0897	1240	270.1	.60
2316	1208	749	459	6.80	633	4.292	.0897	1241	270.3	.59
	1213	752	461	6.99	621	4.342	.0886	1240	269.0	.60
2340	1212	748	464	6.96	621	4.319	.0903	1249	269.3	.61
	1203	749	454	6.88	616	4.235	.0889	1227	270.3	.68
2364	1203	749	454	6.87	615	4.226	.0891	1227	270.3	.67
	1209	751	458	6.96	616	4.287	.0900	1243	271.4	.65
2388	1208	751	457	6.97	617	4.302	.0893	1240	271.3	.63
	1205	752	453	6.93	612	4.240	.0877	1219	269.3	.65
2412	1202	750	452	6.84	615	4.204	.0874	1213	268.3	.60
	1201	749	452	6.96	600	4.176	.0872	1207	267.0	.66
2436	1200	750	450	6.98	598	4.171	.0867	1203	267.0	.66
	1205	751	454	6.89	614	4.228	.0867	1211	266.5	.70
2460	1204	751	453	6.89	612	4.214	.0862	1206	264.9	.65
	1206	751	455	7.02	601	4.216	.0859	1204	264.8	.63
2484	1203	749	454	6.86	616	4.226	.0892	1228	270.0	.61
	1204	750	454	6.88	616	4.238	.0891	1229	270.7	.60
2508	1208	751	457	6.96	619	4.308	.0892	1240	271.3	.62
	1209	751	458	6.99	618	4.319	.0891	1241	270.9	.63
2532	1213	752	461	7.01	620	4.346	.0884	1240	268.9	.65
2556	1212	750	462	6.98	621	4.335	.0888	1241	268.6	.67

Test completed and generator cooled to room temperature.

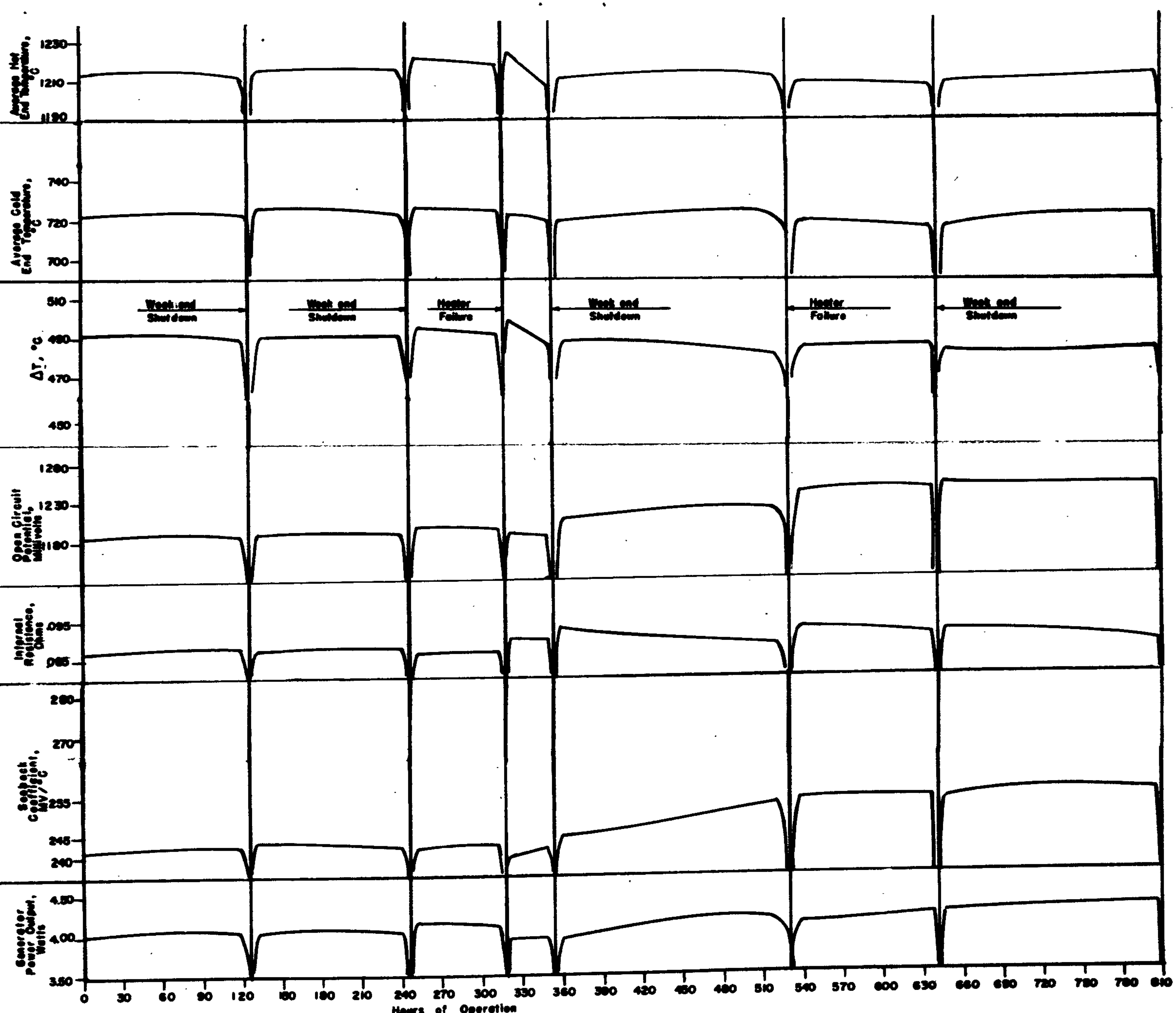


Figure 4. Plots of data for the sustained performance tests on the experimental model generator.

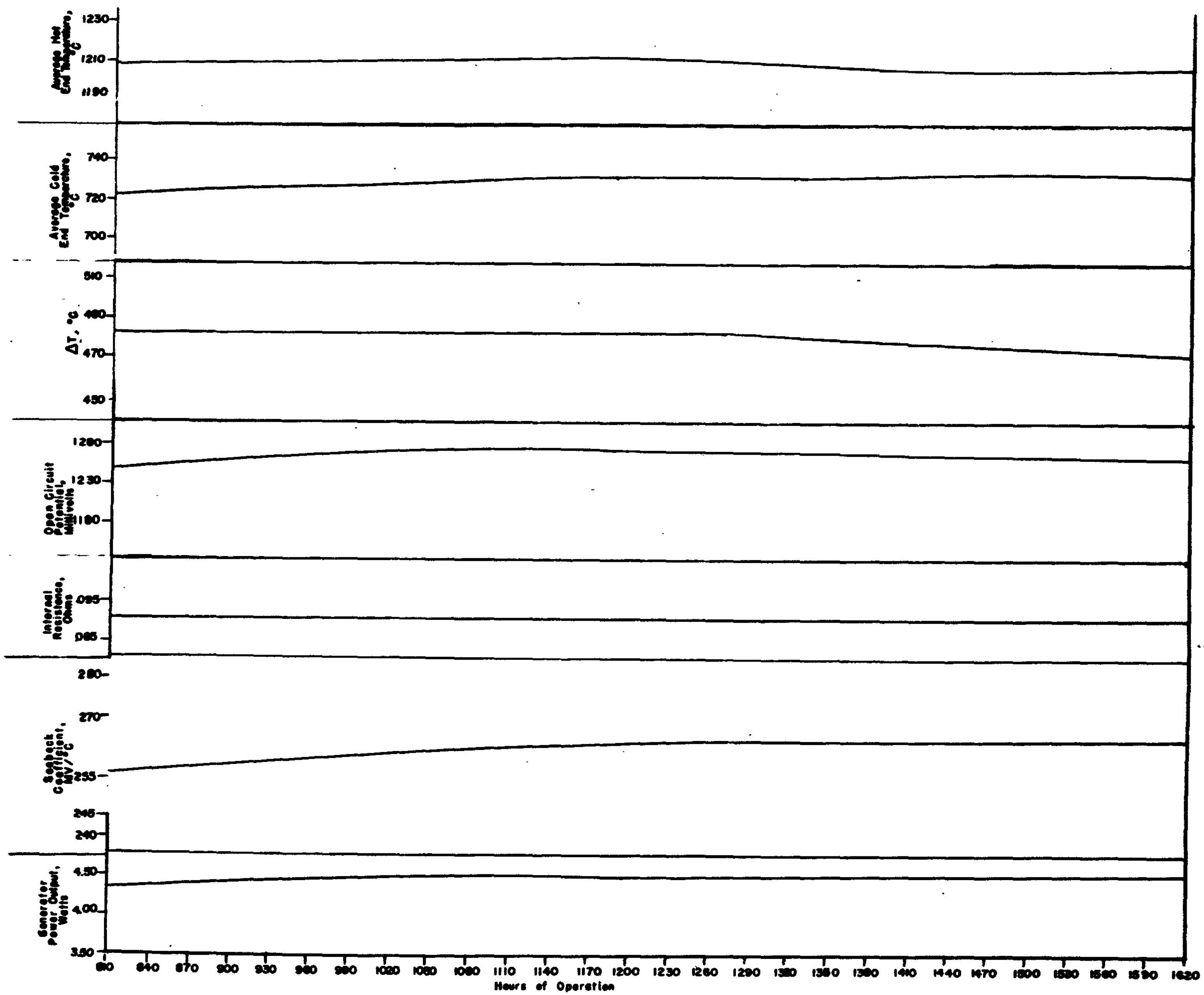


Figure 4. (Cont'd) Plots of data for the sustained performance tests on the experimental model generator.

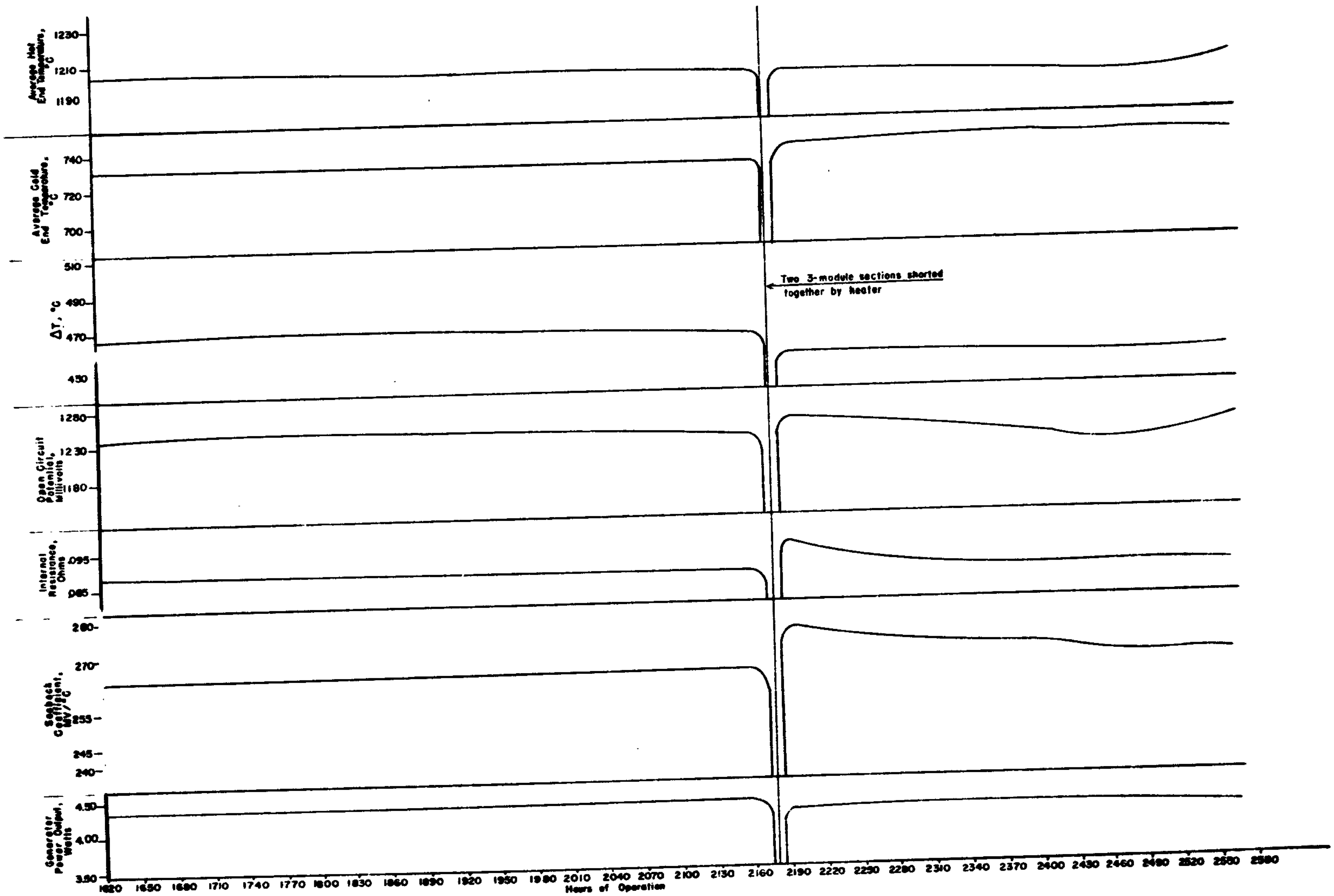


Figure 4. (Cont'd) Plots of data for the sustained performance tests on the experimental model generator.

in generator output with time resulted from the gradual lowering of resistance of the junctions between the modules with time at elevated temperatures in a vacuum. Some improvement in thermo-electric properties of MCC 50 with time may also have occurred.

Examination of the exterior of the generator, at the end of the test, revealed no damage from sublimation, thermal cracking or diffusion damage of its MCC 50-molybdenum couples. Figure 5, a photograph of the generator taken at the end of 2556 hrs exposure to test conditions, may be compared with Figure 3 (at start of test). The exterior of the modules and other generator parts were not visibly affected, other than a darkening of the Fiberfrax insulation. This darkening, previously noted during the 100-hr test last year, apparently has little effect on the thermal and electrical properties of Fiberfrax.

Following completion of the sustained performance test, attempts were made to determine whether a graphite-phenolic radiator coating would increase ΔT's along the generator modules. Attempts were also made to measure drift of the control thermocouples during the 2556-hr test period. The emissive coating evaluation showed that its use on the advanced model should produce an increase of at least 40 °C above the Δ T's obtained on the modules of the experimental model generator. Details of tests on the emissive coatings are presented in section II B 3 , Emissive Coatings.

To determine the possible change (drift) of the thermocouples in 2556 hrs exposure to vacuum and high temperature, careful attempts were made to remove the test-worn thermocouples so that their emf output could be compared with the output of new calibrated ones. Unfortunately, none of the tungsten-rhenium couples used for measuring T_h could be removed intact. When it was found that the old thermocouples were so fragile, a new one was carefully installed in place of the first couple and the generator returned to operation at a T_h of 1200 °C. This procedure permitted comparing the emf's of the used tungsten-rhenium couples against the new one. This sort of a comparison was made again after a second hot-end thermo-couple was replaced, permitting comparison of the T_h of the generator with two new couples and one of the original couples. These tests indicated that the maximum drift of the tungsten-rhenium couples was less than ± 10 °C at 1200 °C after 2556 hrs.

After conducting T_h thermocouple drift evaluation tests on the experimental model generator, two of the cold-end thermocouples were removed intact. These will be compared against new ones to determine how much their calibration may have drifted during the sustained performance test.

If time and project scheduling permit, it is planned to operate the experimental model generator in a vacuum to temperatures of 1300 °C for 500 hrs. If the generator survives this test, the temperature will be increased to 1350 °C. If it survives the 1350 °C test, the temperature would be increased to 1400 °C. Prior to

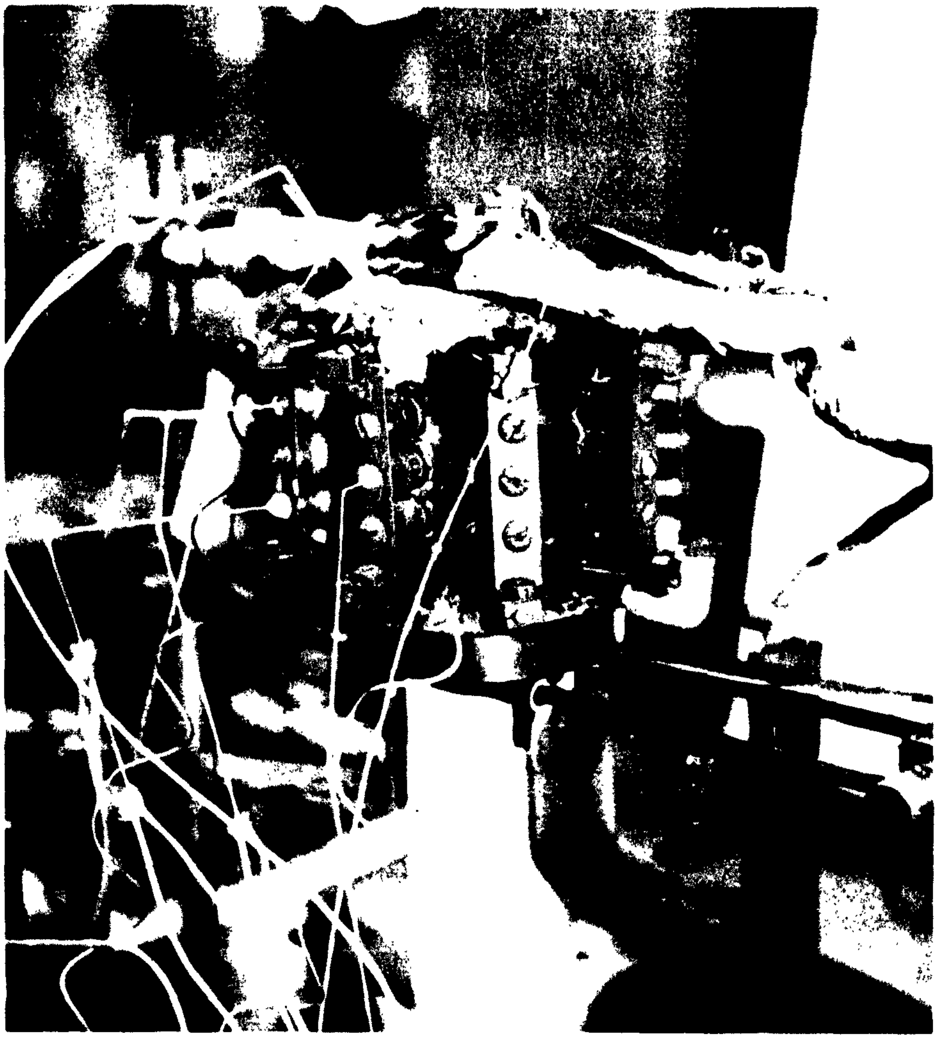


Figure 5. Appearance of experimental model generator after 2556 hrs exposure at a T_h of 1200°C in a vacuum of 10^{-5} - 10^{-6} mm Hg.

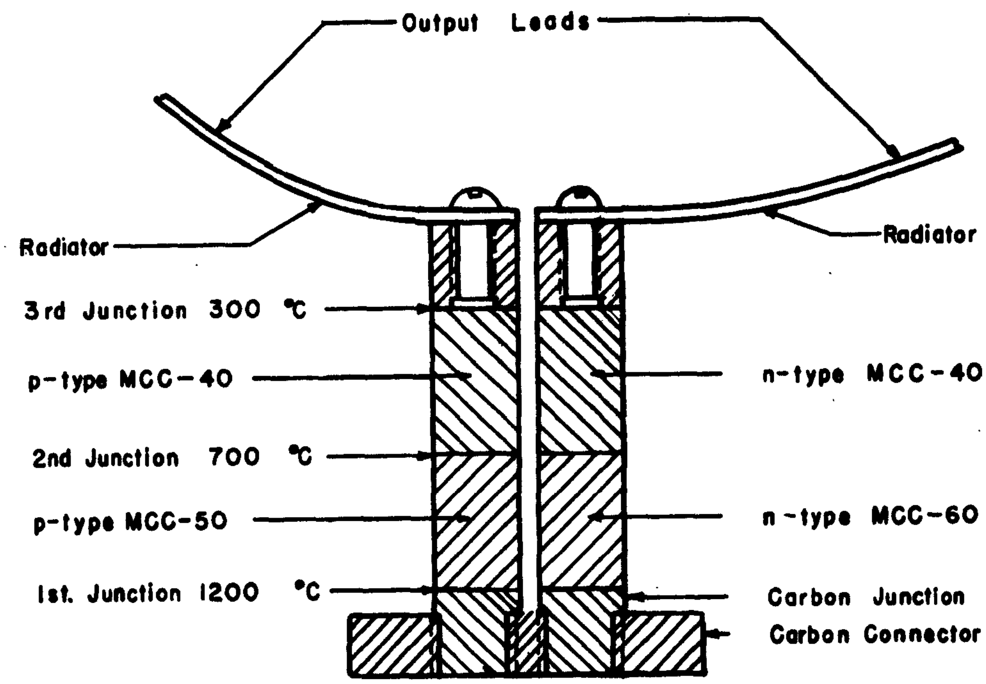


Figure 6. Proposed arrangement of segmented p- and n-type materials for use in an advanced experimental model generator.

starting the 1300 °C test, the worn tungsten heater unit will be replaced with a new one. At that time, a partial inspection of the generator will be made. These plans were made in cooperation with the project engineer.

B. PHASE II COMPONENT IMPROVEMENTS AND EVALUATION

The purpose of this phase is to provide the improved materials and techniques necessary to meet the design goals for an advanced experimental model thermoelectric generator capable of a nominal output of 50 watts, 6 volts, 7% efficiency, 20 watts/lb with less than 10% degradation when operating at temperature for a 1-year period. Operating conditions are to be: a hot junction temperature of 1200 °C and cold junction temperature obtained by radiation cooling in a vacuum of 10^{-5} mm Hg. The 50-watt unit should also accommodate one or more 12" long x 7/16" diameter heat sources representing a portion of a hot liquid metal loop from a nuclear reactor heat source.

To achieve these goals, matching and improvement of the thermoelectric properties of new materials, originated by Monsanto Chemical Company (MCC) to supplement MCC 50, are needed. In addition, segmenting of these new materials in p-n couples, as illustrated in Figure 6, was proposed.

The three supplementary MCC thermoelectric materials to be investigated in addition to improving MCC 50 under this phase of the project are:

1. n-type MCC 60, a new proprietary thermoelectric material useful to 1200-1500 °C and so far the best candidate material for use with p-type MCC 50.

2. n- and p-type MCC 40, new materials useful at temperatures below 850 °C.

To improve the power/weight ratio and efficiency of the advanced experimental generator, a radiator coating of improved emissivity (relative to the nickel oxide coating on the radiators of the 5-watt generator) is needed. Additionally, improved junction forming techniques to permit fabrication of the segmented type modules shown in Figure 6 of low interface resistances and good mechanical properties, are needed. Waste heat radiators integrally joined to segmented modules are also needed. Arc-plasma techniques for forming such radiators and for producing large doughnut or ring-type modules to minimize generator heat leaks are to be investigated.

Preferably, all candidate improvement formulations would be screened in module form. However, the effort required to match and bond junction materials with improved thermoelectric formulations

was clearly beyond the scope of this project. As described on page 14 and in Figures 6, 7 and 8 of the Fourth Quarterly Project Report, special apparatus was designed and fabricated for screening those hot pressed elements (without junctions) of thermoelectric materials not readily fabricated as modules (with thermal and electrical junctions). Apparatus used to evaluate materials in module form was described on page 14 and in Figures 8, 11 and 12 of the Fourth Quarterly Project Report. Both types of apparatus were capable of evaluating materials under the same vacuum (10^{-5} - 10^{-6} mm Hg) and temperature ($\sim$1200°C) conditions.

Details of the work completed under this phase of the project are presented next.

1. Improvement of MCC 50

During the preceding quarter, the effect of additives on the thermoelectric properties of MCC 50 was further evaluated using a module of MCC 50 as the standard. Eighteen modules were fabricated and screened using this MCC 50 formula, modified with various additives and combinations of additives, selected from prior data (Table 3 of the Fourth Quarterly Report. Of this group, 9 showed sufficient promise of improved thermoelectric properties to merit further consideration. Additional modules of each of these formulations were made and subjected to a second evaluation. The results of each evaluation of these modified MCC 50 formulations are presented in Table 2. As shown in this table, results for each module were in all cases better than the MCC 50 formulation module used as the standard in these evaluations. Modules containing osmium boride and calcium oxide additions offered the most immediate promise for improvement in the power generating properties of MCC 50.

Accordingly, further efforts were made to determine the effects of osmium boride and calcium oxide as individual additives and in various combinations of the two. Modules were made from the standard MCC 50 formulation at six different levels of calcium oxide addition: 0.1, 0.3, 0.5, 0.7, 0.9 and 1.0 mole %. Power output per module ranged from a high 0.36 watt at 1.0 mole % calcium oxide to a low of 0.260 watt at 1.1 mole % calcium oxide. All measurements of module properties were made in a vacuum with a hot junction temperature of 1200°C and using the same radiator to cool the cold junction.

Modules were made using seven levels of osmium boride addition: 0.1, 0.3, 0.5, 0.7, 0.9, 1.0 and 1.2 mole %. The same standard MCC 50 formulation was used for this osmium boride series of modules as was used for the calcium oxide series. Power output per module for the osmium boride series ranged from a high 0.3 watt at 0.9 mole % osmium boride to a low of 0.20 watt at 0.1 mole % of the boride.

Table 2. EFFECT OF ADDITIVES ON THE THERMOELECTRIC PROPERTIES OF MODULES OF AN MCC 50 FORMULATION

Module	Additive, mole %	First Evaluation* Module Resistance, ohms	First Evaluation* ΔT Across Module, °C	First Evaluation* Power Output, watts	Second Evaluation* Module Resistance, ohms	Second Evaluation* ΔT Across Module, °C	Second Evaluation* Power Output, watts
Control **	None	0.024	503	0.15	0.024	504	0.15
2	15.75 SiC	0.007	488	0.22	0.007	465	0.20
5	3.5 MgO	0.008	550	0.25	0.008	540	0.24
7	1.0 TiB_2 + 1.0 $MoSi_2$ + 1.0 YB_2 + 1.0 BeO	0.015	587	0.24	0.016	580	0.24
8	0.9 OsB	0.010	611	0.35	0.011	590	0.28
9	0.5 U_3N_4	0.008	560	0.28	0.009	565	0.26
10	1.0 OsB + 1.0 P, 1.0 ZrB_2 + 1.0 Mg-B	0.012	590	0.31	0.014	5	0.26
14***	3.0 OsB	0.007	548	0.30	0.008	555	0.27
15	3.0 OsB + 3.0 CaO	0.009	542	0.24	0.009	545	0.24
16	1.0 CaO	0.009	591	0.36	0.009	580	0.33

* All tests made with the hot end of the module at 1200°C

** MCC 50 formulation used in the experimental model (5 watt) generator produced modules that produced from 0.2 - 0.3 watts at 1200°C

*** Measurements corrected for geometry variations between specimens

Several modules made with combinations of calcium oxide and osmium boride were evaluated at 1200°C and it was indicated that the beneficial effects of these two compounds were not additive in improving MCC 50.

Based on results to date, it appears that the power generating properties of modules of the MCC 50 formulation used in the experimental model generator can be upgraded from an average 0.25 watt to 0.3 - 0.36 watt at 1200°C. This is an improvement of about 25% on an individual module basis. However, it is doubtful, due to interface resistance losses and fabrication variables, that this improvement will exceed 20% when MCC 50 and p-type MCC 40 are joined into segmented modules.

A 1 mole % calcium oxide-MCC 50 composition will be used as the high temperature portion of the segmented MCC 50-MCC 40 (p-type) leg of the p-n couples for the advanced experimental generator. While further improvements in the power generating performance of MCC 50 may be possible, it is recommended that no further effort be made to improve MCC 50 during the remainder of this 12-month project.

2. Improvement of Supplementary Materials

Difficulties continued to be encountered in producing sound, mechanically bonded MCC 60 and MCC 40 modules. Even so, substantial progress was made this quarter in improving the properties of graphite-ended modules of MCC 60 (n-type) and MCC 40 (n- and p-type) thermoelectric materials. In addition, the first segmented couple, consisting of a p-type MCC 50-MCC 40 module and an n-type MCC 60-MCC 40 module, was fabricated and partially evaluated. A more emissive radiator coating was also evaluated and found superior to the nickel oxide used on the radiators of the 5-watt generator.

<u>a. MCC 60 Materials</u> p- and n-type formulations of MCC 60, for use between 1200°C-1500°C, were investigated during the preceding quarter. It was then concluded that p-type MCC 60 would not be as useful as MCC 50, so attempts to further improve the material during this sixth quarter were dropped in favor of concentrating on n-type MCC 60. Of the following elements and their compounds, selected for study with MCC 60, boron, germanium and manganese were rejected on the basis of unfavorable effects on the thermoelectric properties of MCC 60:

antimony	carbon	magnesium	osmium
boron	cobalt	magnesium	silicon
calcium	germanium	nickel	thorium

Forty-two modules of MCC 60, modified by various combinations of antimony, calcium, carbon, cobalt, magnesium, nickel, osmium, silicon and thorium or their compounds (largely oxides), were made and compared for power generation output in a vacuum at ~ 1200 °C. Compounds of calcium, thorium, silicon and cobalt produced the most promising n-type MCC 60 modules. Only modules with these additives produced more than 0.01 watt with a T_h of 1200 °C, the minimum power output considered worthy of further study. Table 3 presents data on the MCC 60 modules that passed this screening test.

On the basis of this work, and in conjunction with the project engineer, it was decided to forego further studies of the effect of additives based on antimony, carbon, magnesium, nickel and osmium. Compounds of these elements showed little promise of upgrading n-type MCC 60 beyond an 0.02 watt level.

Concentrated effort to improve n-type MCC 60 with the silicides of thorium and cobalt in combination with calcium oxide resulted in module 16P of Table 3. It produced 0.08 watt, the highest power output for a MCC 60 module produced to date on this project.

Based on the performance of module 16P, n-type MCC 60 should be used above 850 °C and our previous target of 0.2 watt at 1200 °C for a ΔT of 550 °C should be revised to 0.1 watt at 1200 °C for a ΔT of 350 °C. MCC 40 (n-type) modules, which are appreciably more effective than MCC 60 (n-type), would be used in segmented modules at temperatures of 850 °C and lower. The actual ΔT, over which each segment of thermoelectric (MCC 50, MCC 60 or MCC 40) material should operate to produce the most power per unit of weight in the advanced experimental model generator will be determined by trade-off studies of Joule heat losses, thermoelectric properties of module materials, and radiator characteristics.

Table 3. TESTS ON GRAPHITE-ENDED MODULES OF MCC 60 MODIFIED WITH ADDITIVES

Module No.	Additive, mole %	Seebeck Coefficient, μv/°C	Module Resistance, ohms	ΔT Across Module, °C	Power, watts
16B	4.9 $CoSi$; 1.5CaO 0.5 $ThSi_2$; 0.1 Sb	-120.4	0.017	528	0.059
*16D	2.0 CaO	-148	0.0734	470	0.022
*16E	3.0 CaO	-119.4	0.0456	447	0.021
16F	4.0 CaO	-113.8	0.0178	459	0.079
*16G	5.0 CaO	-183.8	0.0706	460	0.025
*16H	5.0 CaO; 5.0 CoSi	-98.07	0.0226	437	0.029
*16J	3.0 CoSi	-77.7	0.102	476	0.031
16K	5.0 CoSi	-39.0	0.0436	513	0.010
16L	1.0 $ThSi_2$	-86.1	0.0679	569	0.0191
16M	3.0 $ThSi_2$	-30.1	0.0082	428	0.042
*16Q	1.0 As, 4.0 CaO	-120.7	0.0590	420	0.015
16R	1.0 CaO; 1.0 CoSi, 1.0 $ThSi_2$	-71	0.010	429	0.08

*Tested as thermoelectric element without junctions.

b. MCC 40 Materials At the start of this quarter the power output targets for n- and p-type graphite-ended MCC 40 modules presented below was based on a conservative estimate that this thermoelectric material could not be used above 700°C.

Table 4. TARGET VALUES FOR p- and n-TYPE MCC 40 THERMOELECTRIC MATERIALS

Module	T_h, °C	ΔT, °C	Module Resistance, ohms	Power, watts
p-Type MCC 40	700*	300*	0.010*	0.35*
	850**	400**	0.010**	0.35**
n-Type MCC 40	700*	300*	0.010*	0.30*
	850**	400**	0.010**	0.45**

* Target values believed feasible at beginning of project.
** Revised target values based on more realistic estimates of actual output of modules, adjusted to the use of MCC 40 materials to 850°C, instead of 700°C.

The target T_h, Δ T, and power output for MCC 40 modules, shown above, were revised when it became obvious that MCC 40 material can more effectively produce power at temperatures to 850°C, than MCC 50 or MCC 60. Further, as shown under Sustained Testing, section II B5 below, the sublimation losses of MCC 40 materials are low enough to permit their long time operation in high vacuums at 850°C.

Difficulties continued to be encountered this quarter in bonding graphite to MCC 40 elements. Even so, it was possible to produce the modules needed to evaluate the effect of arsenic, boron, bismuth, cesium chloride, antimony and silica as additives on the thermoelectric and power producing properties of MCC 40. Antimony and bismuth had an adverse effect on MCC 40. The results of attempts to determine optimum compositions of p- and n-type MCC 40 modules by varying their silica, cesium chloride, boron and arsenic content are presented in Table 5.

As shown in this table, the best p-type MCC 40 formulation to date, for use at 850°C, is one utilizing a 1 mole % silica addition. Its power output of 0.233 watt, resistance of 0.0161 ohm at 850°C T_h, and a ΔT of 415°C is below the revised target power output (Table 4) of 0.35 watts.

The best n-type MCC 40 formulation for use at 850°C is one containing 2 mole % arsenic and 1 mole % thoria. Its power output of 4.494 watt, resistance of 0.0084 ohm at 850°C T_h and a Δ T of 419.8°C exceeds the target values of 0.45 watt and tends to offset the lower-than-desired output for p-type MCC 40.

The power outputs attainable for p- and n-type MCC 40 modules encouraged us to proceed with efforts to fabricate graphite-ended and segmented modules of MCC 50-MCC 40 (p-type) and MCC 60-MCC 40 (n-type) for evaluation purposes. Details of the promising results obtained with the resulting p-n couple are discussed under Junction Forming, section II B4, of this report.

In our opinion still further improvements in the power generating properties of n- and p-type MCC 40 modules can be attained. Further studies of the effect of various concentrations of boron, silica, calcium oxide, and thoria content in p-type MCC 40 are underway and will continue into the next quarter. Studies to further optimize the arsenic and thoria content of n-type MCC 40 are also continuing.

Table 5. TESTS ON GRAPHITE-ENDED MODULES OF n- AND p-TYPE MCC 40

Module Type	Additive, mole %	Seebeck Coefficient, µv/°C	Module Resistance, ohms	ΔT Across Module, °C	Power Output, watts
p	SiO_2, 0.5	310.0	0.0172	436.2	0.218
p	SiO_2, 1.0	323.5	0.0161	415.0	0.233
p	SiO_2, 2.0	306.0	0.243	451.2	0.165
p	CsCl, 0.5	262.8	0.0159	478.0	0.203
p	CsCl, 2.0	258.8	0.0106	423.8	0.223
p	B, 0.25	297.6	0.0148	436.5	0.233
p	B, 0.125	289.5	0.0155	430.6	0.204
n	As, 3	260.0	0.0114	436.8	0.348
n	As, 4	244.3	0.0091	455.2	0.424
n	As, 2.0 + ThO_2, 1.0	278.8	0.0084	419.8	0.494
n	As, 2.0 + CaO, 1.0	293.3	0.0140	430.5	0.340
n	As, 2.0 + SiO_2, 1.0	268.1	0.0088	441.0	0.480

3. Emissive Coatings

During the preceding quarter, use of a commercially available silicone-aluminum-toluene coating product was investigated as a means of increasing the heat rejected from the radiators of the 5-watt generator. While this coating offered promise of higher emissivity than the nickel oxide coating on the small copper radiators used on the experimental generator, it tended to flake and peel in a vacuum at the 700°C cold junction (radiator) temperatures encountered. Further, the aluminum in this coating alloyed with the copper radiator, lowering its thermal and electrical conductivity. These two difficulties detracted from the silicone-aluminum-toluene coating and further work on it was abandoned.

Experiments with various suspension agents led to a graphite-phenolic varnish base coating having promising emissivity (on a relative basis) and good adherence on copper metal. This material, diluted with ethyl alcohol, could be painted on the radiators and required only air drying for 24 hrs followed by a low (50-200°C) temperature bake of 2 hrs in air or an inert atmosphere. From the test results (using a simple comparator flowmeter), it was predicted that this coating would produce an increase of 30-60°C in the temperature drop across modules mounted in the 5-watt generator.

After completing 2556 hrs operation on the experimental generator, it was decided to determine the effect of this coating on the ΔT across modules of the 5-watt generator. This could be accomplished more meaningfully by applying, curing and testing the coating in place on the radiators of the generator. The graphite-phenolic coating was applied directly over and cured on the nickel oxide coated radiators of the generator, with extreme care to prevent any movement of the thermocouples in the hot and cold end of the generator. After completion of the coating operation the generator was returned to a steady T_h of 1200°C. When thermal equilibrium was again achieved, the temperature drop down the length of the modules of the generator had increased by 40°C above the ΔT obtained with the original nickel oxide coated radiator. On the basis of 200-300 hrs exposure to a radiator temperature of $\sim$700°C in a vacuum of 10^{-5} - 10^{-6} mm Hg, the graphite-phenolic coating has shown no appreciable loss of radiating power. It has shown a slight tendency to blister when it was heated too rapidly in a vacuum immediately after application, but this problem should be minimized with a more gradual vacuum bakeout cycle.

Determination of an increase in generator output with the increased ΔT available from the graphite-phenolic coating was not possible as the tungsten heater once again short circuited several of the 3-module generator sections.

Specimens of this coating have been submitted to ASD for quantitative emissivity measurements to $\sim$700°C in a vacuum. The emissivity of other specimens will be measured under an inert atmosphere to $\sim$600°C. Emissivity of this graphite-phenolic coating will also be compared with a high emissivity (0.88 at 700°C in a vacuum) coating known to ASD.

4. Junction Forming

To obtain design data the fabrication of four segmented modules was attempted late this quarter. These modules consisted of MCC 50-MCC 40 (p-type) and MCC 60-MCC 40 (n-type) materials joined together and capped on each end with graphite. One module failed during hot-pressing and one was broken during attempts to equip it with thermocouple holes after being successfully hot-pressed.

The procedure used to fabricate these initial segmented p-type modules consisted of hot-pressing 5 g of MCC 50 powder in a boron nitride-lined graphite die between two graphite (type AUC) end plungers.

The temperature of the die assembly was raised to 2020°C in 5 minutes while applying pressure to 4000 psi. These conditions were maintained for 8-10 minutes. The assembly was then cooled to room temperature and one of the graphite ends was removed. The MCC 50-graphite interface was ground away, exposing a fresh MCC 50 surface on one end of a 0.6" long MCC 50 element section. The diameter of the MCC 50 element was ground to 0.500" and used as a plunger for the hot-pressing of the MCC 40 (p-type) element to MCC 50. The p-type MCC 40 powder mix (5 g) was hot-pressed in a second boron nitride-lined graphite die between an AUC graphite plunger on one end and the MCC 50-graphite plunger on the other. The temperature of the die was increased to 1350°C over a 10-minute period while maintaining a rate of plunger travel of 0.01-0.02"/minute. When compaction of 0.2-0.3" had taken place, the temperature was decreased to ambient while increasing the pressure to 2000 psi. Upon reaching ambient temperature, the die was removed from the hot press and the segmented module was removed. The MCC 50 and the MCC 40 sections of the p-type module, shown in Figure 7, were 0.5" long x 0.5" diameter.

An identical procedure, with the following exceptions, was used to produce the graphite-ended segmented n-type module shown in Figure 8:

(1) Only 4 g of MCC 60 powder was used in place of MCC 50 and a hot-pressing temperature of 2100°C was used instead of 2020°C. The length of the resulting MCC 60 module segment was 0.4" rather than 0.5".

(2) In producing n-type MCC 40, 6.8 g of this powder was used in place of 5 g of p-type MCC 40 and the resulting module segment was 0.6" long rather than 0.5".

The light-colored material on the surface of the segmented p- and n-type modules of Figures 7 and 8 is MCC 40 that was extruded around the MCC 50 and MCC 60 and plungers during hot pressing. It is not necessary to remove this material since it will not harmfully affect the performance of the segmented modules. Its chief effect will be to increase the weight lost by vaporization from segmented modules when a portion of the extruded MCC 40 material is heated above 850°C in a vacuum.

The p- and n-type segmented modules, shown in Figure 7 and 8, are currently being tested as a p-n couple in a vacuum of 10^{-5} - 10^{-6} mm Hg at 1200°C (T_h). The promising results of this test series are presented under Sustained Testing, section II B5, of this report.

As discussed in the Fourth Quarterly Report, the sizeable heat losses and fabrication costs inherent in the initial experimental model generator design could be significantly reduced if sandwich-type

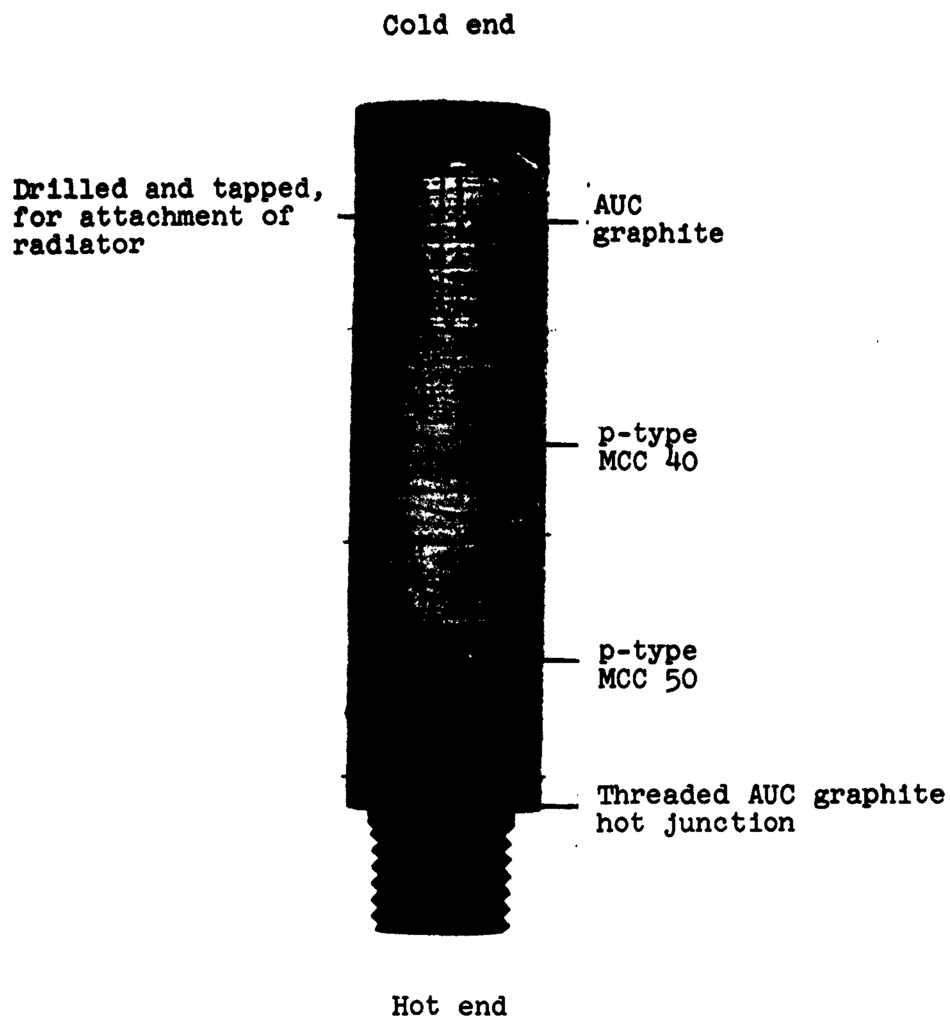
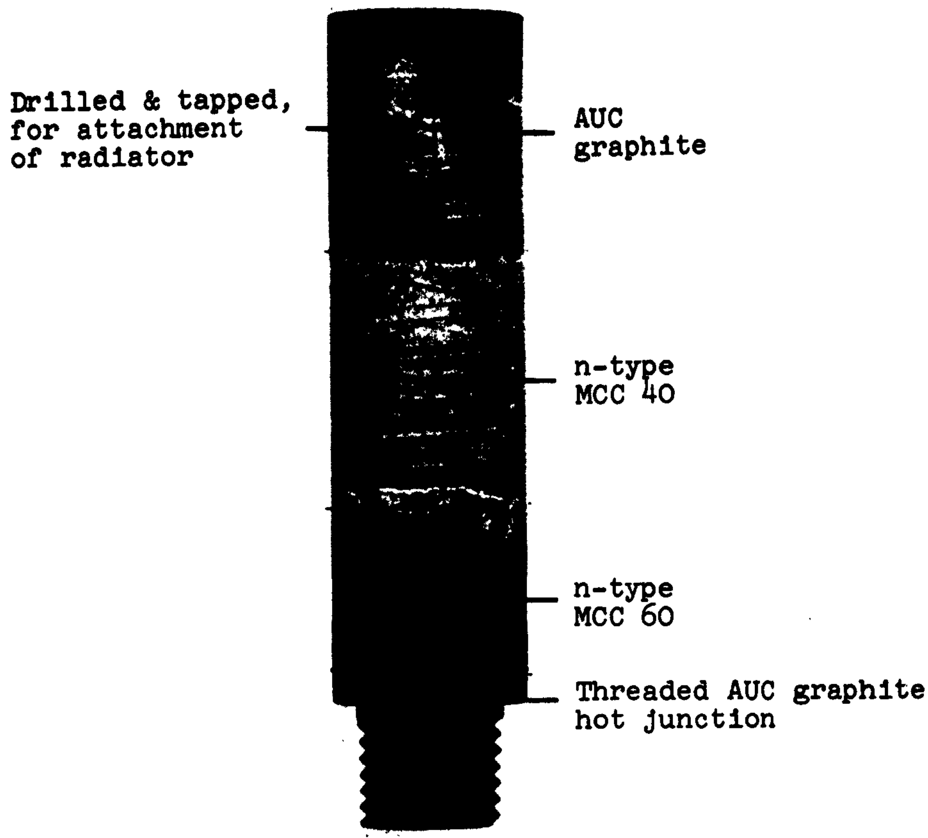


Figure 7. Graphite-ended p-type segmented module of MCC 50-MCC 40.

Cold end



Hot end

Figure 8. Graphite-ended n-type segmented module of MCC 60-MCC 40.

ring-or doughnut-shaped modules of MCC 50 and other thermoelectric materials could be fabricated. Development of arc-plasma spray coating techniques to produce such sandwich-type modules is an objective of this phase of the project. A relative goal is to improve the practicability of producing hot and cold junctions between thermoelectric modules via arc-plasma and flame spraying. Success in the latter would permit significant reductions in the weight of the advanced experimental model generator by eliminating fastening pins or screws and by reducing the length of graphite now required for attachment of junction and radiator materials at the hot and cold ends of modules.

Several sandwich-type MCC 50 modules were fabricated by arc-plasma methods this quarter. One, a graphite-molybdenum-MCC 50-molybdenum module, is shown in Figure 9. Its thermoelectric properties have not yet been measured.

Other sandwich-type modules were evaluated in a vacuum of 1200 °C (T_h) for S, and ΔT characteristics, as tabulated below. Satisfactory electrical contacts to the cold junction of these modules were not accomplished, preventing measurement of their resistance and power output characteristics.

Module No.	Description	Thickness of MCC 50 layer, mils	Seebeck Coefficient, μv/°C	T_h, °C	ΔT Across Module, °C
82	Mo-MCC 50	1/16	308	1192	200
84A	C-Mo-MCC 50	1/16	136	1192	264
86A	C-Mo-MCC 50	1/8	185	1190	350
89A	C-Mo-MCC 50	1/16	266	1187	266

Each of the above modules withstood an ambient-1200 °C-ambient thermal cycle in their evaluation. A thin (2-3 mil) coating of molybdenum was used to improve the bond between the graphite hot junction material and MCC 50 for modules 84A, 86A and 89A. MCC 50 was sprayed directly on graphite to produce module 82. The chief significance of the data from these 4 modules is that sufficiently high Seebeck coefficients and ΔT's were obtained to indicate that useful thermoelectric modules can be made by this approach. It has definite possibilities as a technique for mass production at lower costs and with more useful geometries for meeting generator design problems.

Techniques for attaching cold junction leads for measurement of the power output and resistance of complete modules like that shown in Figure 9 are being investigated. In addition, new batches of MCC 50 powder, with and without calcium oxide additive, are being prepared for use in further development of the arc-plasma method of fabricating sandwich-type modules.

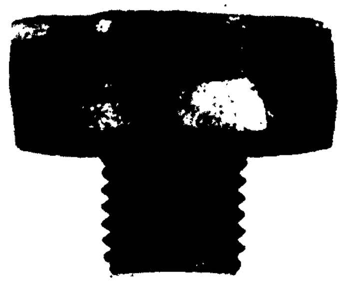


Figure 9. Sandwich-type module 86D made by arc-plasma spray coating a thin coat of molybdenum on the graphite base, followed by a 1/8" layer of MCC 50 and a final cold junction layer of molybdenum.

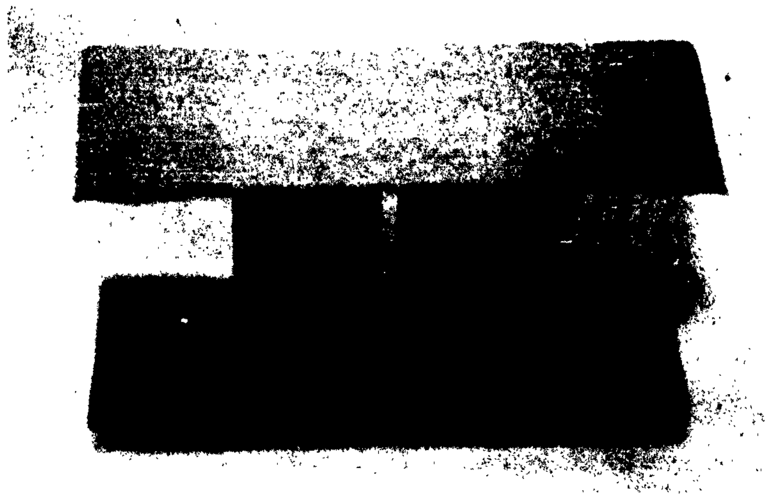


Figure 10. Experimental 2-leg module with arc-plasma spray coated molybdenum hot and cold junctions.

Figure 11. Experimental 2-leg module with arc-plasma spray coated molybdenum cold (radiator) junction.

An investigation was initiated this quarter of ways of utilizing arc-plasma and flame coating techniques to provide strong, thin, and lightweight hot and/or cold junctions between legs of p-n couples. Such junctions could be used in place of long and heavy graphite-molybdenum hot-junction shoes and graphite-copper radiators employed on the 5-watt experimental generator. If this approach is successful, high power/weight ratios for the advanced experimental model generator will be possible. Promising results in this effort were obtained, as shown in Figure 10. Here, two short graphite cylinders, simulating graphite-ended segmented thermoelectric modules joined at their hot and cold ends by plasma-sprayed molybdenum, are shown. A second example is presented in Figure 11 showing two short graphite cylinders joined at one end (the radiator end) by plasma-sprayed molybdenum. This technique also offers high promise of adaptation to mass production techniques and high power/weight ratios. However, more effort is needed to evaluate the mechanical strength, thermal shock resistance, and thermoelectric properties of junctions made this way.

5. Sustained Testing

The most important milestone on this phase during the past quarter was the initiation of sustained testing on the first p-n couple fabricated from the module shown in Figures 7 and 8. As shown in Figure 12, individual p- and n-type modules were screwed into a combination graphite hot-junction heat source unit. The hot-junction unit is heated by a tungsten wire heater (not shown) wound around the vertical post below the large diameter-threaded portion of the unit. The two modules shown in Figure 12 represent typical modules, not the p-n couples on which the data in Table 6 was collected.

Figure 13 shows the p-n couples mounted on graphite within a multiwall radiation shield unit. The p-type MCC 50-MCC 40 leg or module is the longest one shown. Coated-copper radiators, module power leads, and the top of the heat shield unit are not yet installed. An 0.005" x 1" x 1 1/4" molybdenum sheet (light-colored metal strip shown at the bottom or hot end of module) is used to lower the resistance of the hot junction end of the couple. Alumina-insulated tungsten-rhenium thermocouples, which measure the hot-end temperature, extend horizontally through the shields and outward from the graphite heat unit. Figure 14 shows the completed test configuration for the sustained evaluation tests on the p-n segmented couple reported in Table 6.

The power output of the p-n couple shown in Figure 13 was 0.96 watt with a ΔT of 797°C for a T_h of 1214°C. This is encouragingly high. While it is not expected that a ΔT of 760-800°C can be obtained on the advanced generator, it is likely that ΔT's in the neighborhood of 600-650°C (corresponding to radiator temperatures of 550-600°C) can be achieved. With a 550-600°C ΔT and a T_h of

Figure 12. Typical graphite hot-end junction configuration for evaluating graphite-ended p-n couples.

Figure 13. Partial test configuration used to evaluate graphite-ended segmented p-n couple showing modules joined with 0.005" x 1" x 1 1/4" molybdenum and graphite hot junction and surrounded by radiant heat shields.

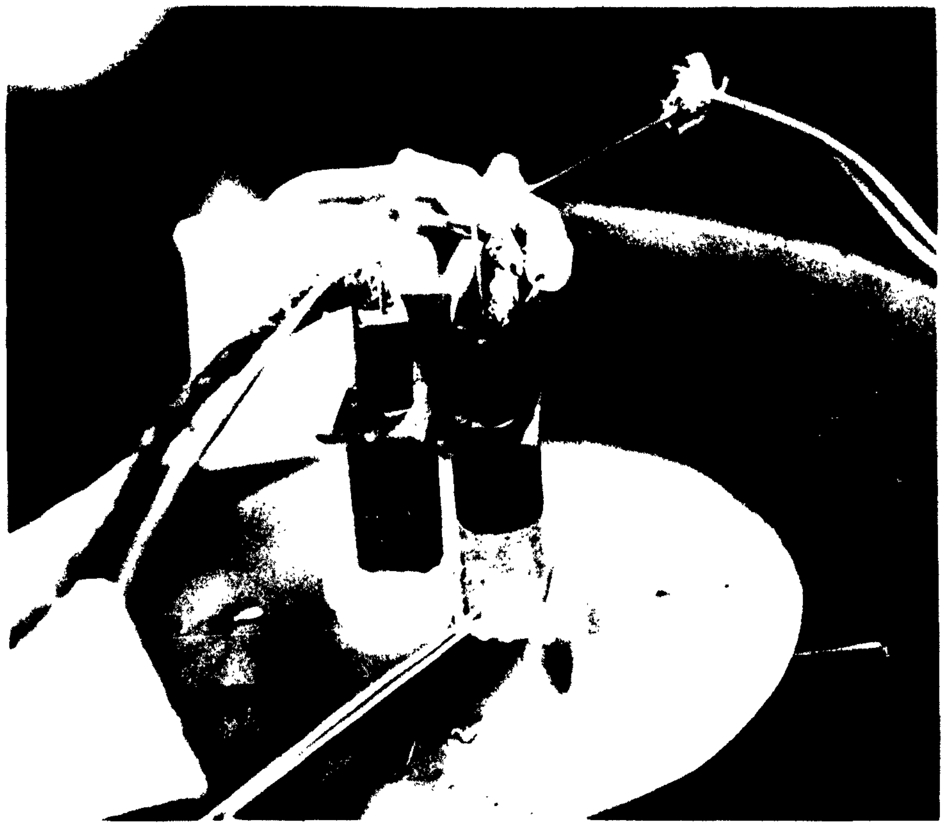


Figure 14. Completed test configuration used to conduct sustained evaluation tests on p-n couples.

Table 6. TEST DATA ON GRAPHITE-ENDED p-n SEGMENTED COUPLE

Hours of Operation	Average Hot End Temperature, °C	Average Cold End Temperature, °C	Average ΔT Across Couple, °C	Couple Characteristics Under Approximately Matched Load				Open Circuit Potential, mv	Seebeck Coefficient µv/°C	Vacuum, mm Hg x 10^{-5}
				Current, amp	Potential, mv	Power, watts	Internal Resistance ohms			
1	1176	417	759	4.56	162.5	.741	.0359	326.4	430.0	.56
16	1178	409	769	4.87	167.6	.816	.0357	341.5	444.1	.40
36	1173	408	765	4.93	170.7	.842	.0353	344.7	450.6	.20
58	1171	408	763	5.00	170.5	.852	.0354	347.6	455.5	.20
64	1173	408	765	5.01	170.5	.854	.0354	348.0	454.9	.20
90	1174	409	765	5.00	172.8	.863	.0354	349.8	457.3	.20
92	1192	412	780	5.09	178.4	.908	.0349	356.2	456.7	.38
110	1201	415	786	5.12	180.6	.925	.0348	358.6	456.2	.45
117	1200	414	786	5.10	180.9	.923	.0347	358.0	455.5	.30
134	1214	417	797	5.21	184.2	.960	.0346	364.3	457.1	.30
141	1200	417	783	5.13	184.9	.948	.0341	359.8	459.5	.30
159	1200	406	794	5.12	183.2	.938	.0354	364.7	459.3	.30

Tests Continuing

~1200 °C, it is anticipated that a power output of 0.7 watt per couple will be feasible for the advanced experimental generator. On this basis, the advanced generator should produce 250% more power per module than was possible with the 5-watt model.

Since the test is continuing, sublimation losses cannot be determined on each of the modules. This information will be obtained after 250 hrs operation. The fact that power generating properties have not decreased with time indicates that no serious sublimation or diffusion damage has yet occurred. Tests on the p-n couple, Figure 13, are continuing. As further improvements in the thermoelectric properties of segmented couples are attained, couples of such improved materials will be subjected to sustained evaluation tests.

Sublimation tests on individual single segment modules of MCC 60, MCC 40 (p-type), and MCC 40 (n-type) were also conducted. An MCC 60 module, held at 1200 °C ± 10 °C in a vacuum of 10^{-5} - 10^{-6} mm Hg, showed less than 1.9% vaporization loss in 530 hrs. An n-type MCC 40 module, run at 700 °C ± 10 °C in a vacuum of 10^{-5} - 10^{-6} mm Hg, showed only a 0.12% loss after 450 hrs. This loss was so low that sublimation tests on p-type MCC 40 are being run at 850 °C.

III. CONCLUSIONS

Based on results obtained during the 2556-hr sustained performance test, and the promising developments with n- and p-type thermoelectric materials needed to complement p-type MCC 50, the following conclusions were reached:

1. The power generating properties of MCC 50-molybdenum couples used in the experimental model generator are stable to 2556 hrs operation at T_h 1200 °C (+25 °C-4 °C) in a vacuum of 10^{-5} - 10^{-6} mm Hg. During this test the couples sustained no visible damage from sublimation, diffusion at interfaces, or thermal cracking.

2. Power/weight ratios for the experimental model increased from 2.5 watts/lb at the start of the test to 2.7 watts/lb after 2556 hrs, an 8% gain in power output. This increase probably resulted from lowered junction resistances due to vacuum welding at the cold ends of the MCC 50-molybdenum couples.

3. A more emissive coating, applied over the nickel oxide coated-copper radiators of the experimental model generator, resulted in an increased ΔT of 40 °C.

4. Tests above 1200 °C should be run to determine the top feasible operating temperature for this model.

5. Segmented p-n couples, based on MCC 50-MCC 40, MCC 60-MCC 40 modules when operated at a T_h of 1200 °C, should produce 0.7 watt/couple. An advanced experimental generator equipped with such couples, a more emissive coating and improved junctions should be capable of a 10-20 watt/lb ratio.

IV. FUTURE PLANS

Effort during the next quarter will be devoted to the following areas:

1. Sustained testing of the experimental model generator at temperatures of 1300 °C and higher.

2. Efforts to improve p- and n-type MCC 40 materials and to fabricate and test improved p- and n-type segmented couples.

3. Attempts to further improve junction forming techniques.

4. Development of a design for the advanced experimental model generator.

5. Sustained evaluation tests on the most promising thermoelectric materials in module and/or couple form.